

Supporting Information:

Layered TiS₂ Positive Electrode for Mg Batteries

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Experimental Method

Material synthesis and characterization. Layered TiS_2 was synthesized by a previously reported procedure¹ with slight modifications. Typically, titanium powder was ground with 10% excess sulfur and sealed in an evacuated ($\sim 5 \times 10^{-2}$ mbar) quartz ampule. The mixture was heated at 450 °C for 1 day, followed by a slow ramp to 550 °C in a 2 day period and held for 46 hours. The mixture was quenched in water, reground with additional 5% sulfur, sealed under vacuum in a quartz tube, heated at 1 °C/min rate to 550 °C for 36 hours and quenched in water. X-ray diffraction (XRD) analysis was carried out on a PANalytical Empyrean diffractometer with Cu-K α radiation. Material morphologies were examined using a Zeiss field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy detector (EDX).

Electrochemistry. Electrode preparation and cell assembly was carried out in an Ar-filled glovebox with O_2 and H_2O levels below 5 ppm. Positive electrodes were prepared by mixing the as-prepared material with Super P and polyvinylidene fluoride (PVDF, Sigma-Aldrich, average Mw $\sim 534,000$) in an 8:1:1 weight ratio in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99.5%) and the slurry was casted onto Mo foil. The APC electrolyte was prepared according to the reported procedure,² using tetrahydrofuran (THF) or tetraglyme (G4) as the solvent. Magnesium metal was polished with carbide paper (Mastercraft ®, 180 grit SiC), cleaned with Kimwipe and served as the reference and counter electrode. All electrochemical studies were carried out in 2325 coin cells that were held in thermostatted oven at 60°C and tested on the VMP3 potentiostat/galvanostat (Bio-logic).

XRD studies. The slurry of the positive electrode was cast on a glassy carbon electrode and assembled in a home-made *in-situ* cell. The cell was held in a thermostatted oven at 60°C, cycled on a VMP3 potentiostat/galvanostat (Bio-logic) to the point of interest, removed for XRD scanning and replaced for further cycling. A background broad hump in the range of 15-30 2θ degrees results from the glassy carbon window used on the *in-situ* cell. Cell parameters were exacted by the Le Bail fitting protocol³ using the FullProf suite⁴.

List of Supplementary Tables

Table S1. Cell parameter evolution of layered TiS_2 during electrochemical cycling. Points on the electrochemical profile where XRD analysis was performed are indicated in Figure 3 in the main text.

Point	Phase 1		Phase 2		Phase 3		Phase 4	
	a (\AA^2)	c (\AA^2)	a (\AA^2)	c (\AA^2)	a (\AA^2)	c (\AA^2)	a (\AA^2)	c (\AA^2)
A	3.4058(2)	5.6987(4)	-	-	-	-	-	-
B	3.4079(3)	5.6925(4)	3.416(3)	5.903(7)	-	-	-	-
C	3.4091(5)	5.6955(6)	3.434(2)	5.874(6)	3.431(2)	6.112(3)	-	-
D	3.427(2)	5.696(3)	-	-	-	-	3.4934(5)	6.123(1)
E	3.420(3)	5.696(2)	-	-	3.4273(7)	6.1001(9)	3.4838(5)	6.158(2)
F	3.416(2)	5.702(2)	-	-	3.4412(8)	6.035(3)	3.4881(6)	6.1041(5)
G	3.407(3)	5.706(3)	3.4328(6)	5.973(2)	3.4391(6)	6.1144(6)	-	-

List of Supplementary Figures

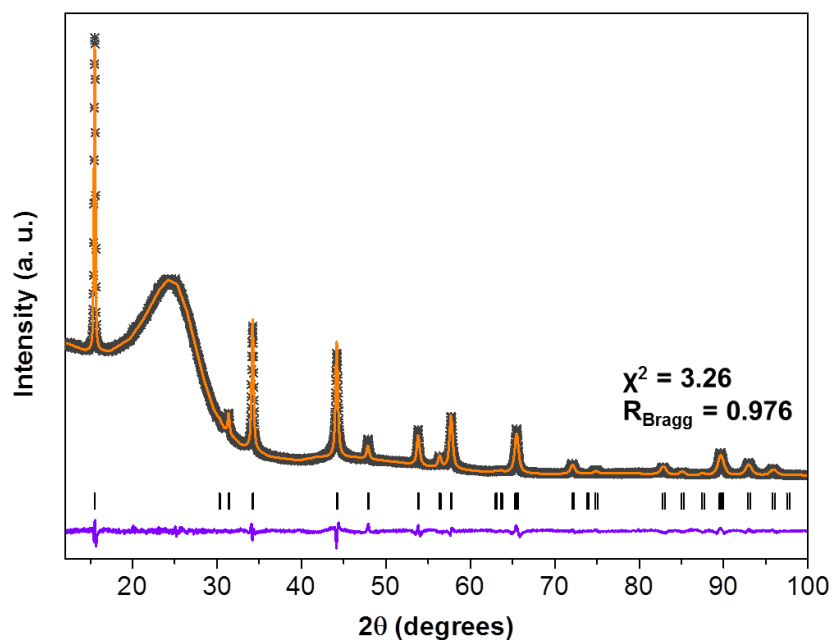


Figure S1. XRD Le Bail (full profile) fitting of TiS_2 . (Grey crosses – experimental data, orange line – fitted data, violet line – difference map between observed and calculated data, black ticks – the $P\bar{3}m1$ phase (phase 1)). The resulting cell parameters ($a = 3.4058(2)$ Å and $c = 5.6987(4)$ Å) agree with the literature values ($a = 3.407(2)$ Å and $c = 5.695(3)$ Å, ICSD #601315).¹ The broad hump is a background signal from the glassy carbon window.

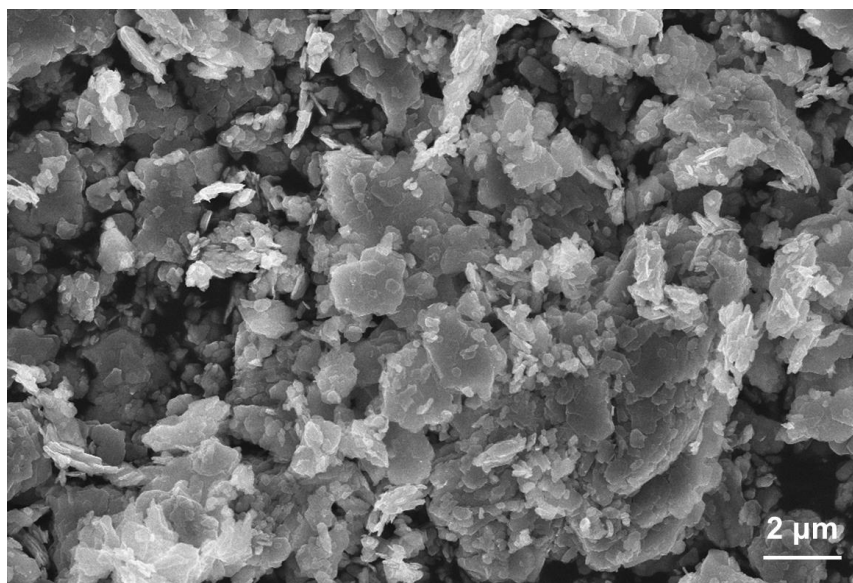


Figure S2. SEM image of TiS₂ showing its platelet morphology.

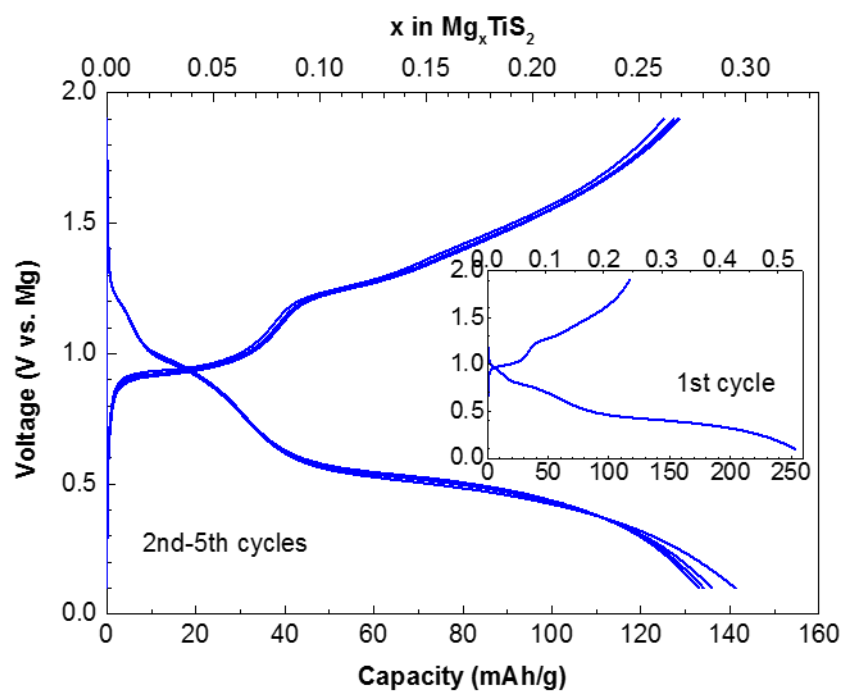


Figure S3. Discharge and charge profiles of TiS_2 tested in coin cells with APC/G4 electrolyte and Mg anode at C/10 and 60 °C.

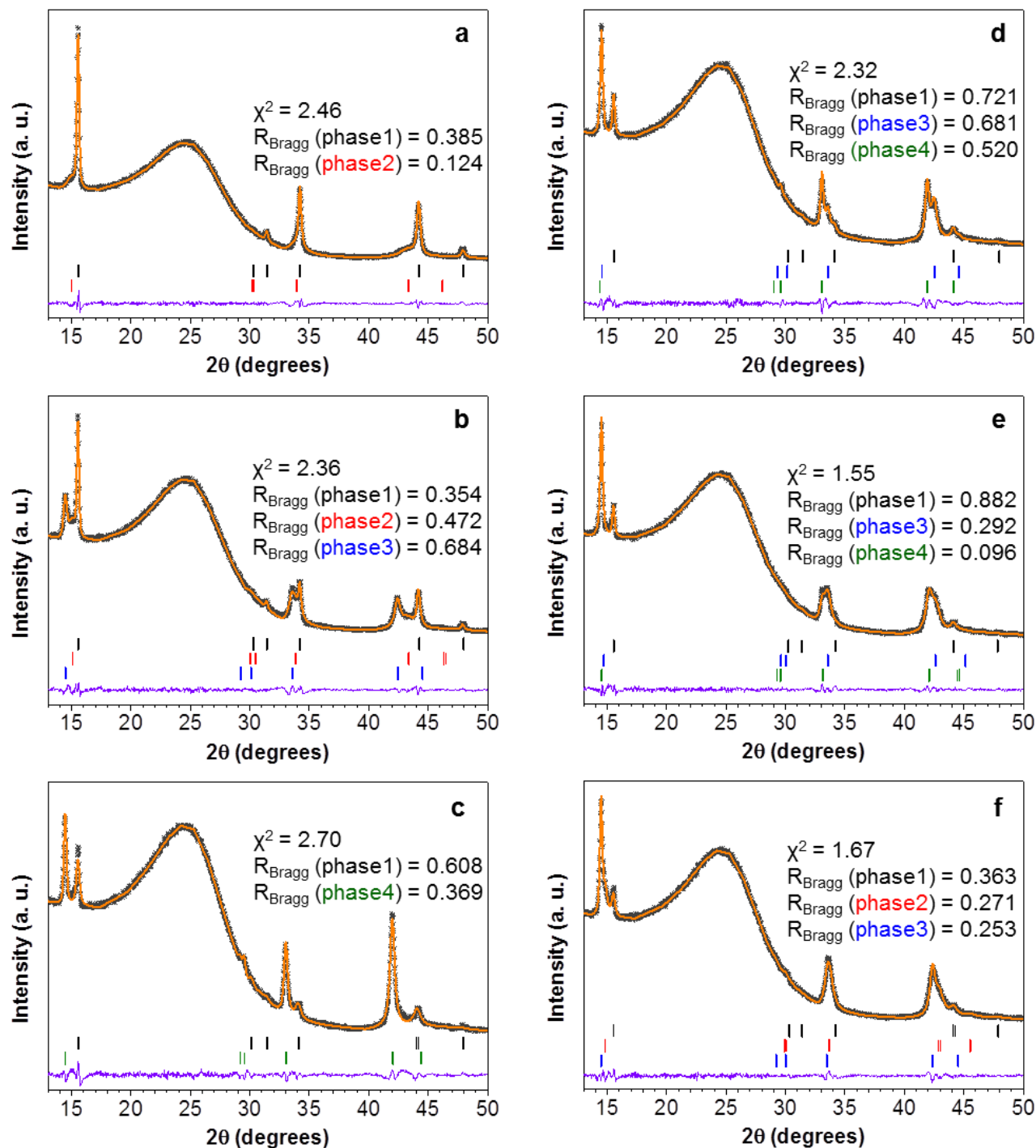


Figure S4. XRD Le Bail (full profile) fitting of TiS_2 at different electrochemical stages: (a) – B, (b) – C, (c) – D, (d) – E, (e) – F and (f) – G (Grey crosses – experimental data, orange lines – fitted data, violet lines – difference map between observed and calculated data, ticks – the $\text{P}\bar{3}\text{m}1$ phases (black – Phase 1, red – Phase 2, blue – Phase 3 and green – Phase 4)). The broad hump is a background signal from the glassy carbon window.

References

- (1) McKelvy, M. J.; Glaunsinger, W. S. Synthesis and Characterization of Nearly Stoichiometric Titanium Disulfide. *J. Solid State Chem.* **1987**, *66*, 181-188.
- (2) Mizrahi, O.; Amir, N.; Pollak, E.; Chusid, O.; Marks, V.; Gottlieb, H.; Larush, L.; Zinigrad, E.; Aurbach, D. Electrolyte Solutions with a Wide Electrochemical Window for Rechargeable Magnesium Batteries. *J. Electrochem. Soc.* **2008**, *155*, A103-A109.
- (3) Le Bail, A. Whole Powder Pattern Decomposition Methods and Applications: A Retrospection. *Powder Diffraction*. **2005**, *20*, 316–326.
- (4) Rodríguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. *Physica B* **1993**, *192*, 55-69.